

Patent No. 626,363

## Production of Titanium by Fused Salt Electrolysis

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9 Claims—No drawing

This invention relates to the electrolytic deposition of metallic titanium. More particularly, it relates to the recovery of titanium by a fused salt electrolysis in which the titanium is provided by a compound of titanium and nitrogen such as titanium nitride.

Various compounds of titanium have been proposed as source materials from which the titanium could be separated by an electrolytic process including the dioxide, monoxide, carbide and various simple and complex halides. Because of the marked tendency of titanium to combine with oxygen, the use of oxygen containing sources is not entirely satisfactory and requires special precautions to insure a high quality product. In electrolyses involving the halides, a free halogen is usually one of the reaction products and a cell product of this nature is extremely corrosive, and may be noxious or toxic to operating personnel. When the carbide is used free carbon may be released into the bath and contaminate the titanium produced.

I have found that when the titanium is provided by titanium nitride, contamination of the deposit is virtually eliminated, cell construction may be greatly simplified and the apparatus may be constructed of inexpensive materials not peculiarly restricted to those providing superior corrosion resistance to moist chlorine or other free halogens.

In the practice of my invention, the metallic titanium is deposited on a suitable cathode by electrolytic decomposition of titanium nitride either as an anode or as a material added adjacent the anode rather than by electrolytic decomposition of a titaniferous bath component. As a consequence the deposition of titanium may be carried out over a long period of time without interruption for replacement of the fused salt bath. In general, the bath should contain at least about 5% by weight of a titanium halide in order to give consistently satisfactory results and although there is no actual limit to the amount of the titanium halide that can be present, I have found that a maximum amount of not more than 25% by weight represents a satisfactory balance between economy and effectiveness of the operation. Any titanium halide may be used for the purpose provided it can be retained in the bath either as a simple halide or as a complex constituent in at least a minimum amount. Thus, although titanium tetrachloride dissolves only slightly in a fused halide salt bath, continued introduction of the tetrachloride into the bath under electrolyzing conditions will effectively build upon the bath a satisfactory amount of a titanium halide. On the other hand, such halides as the tetraiodide, tetrabromide and tetrafluoride; the titanium trihalides and titanium dihalides; and the titanium double fluorides, such as sodium, potassium or lithium fluotitanate may all be used as direct additives to the bath or may be formed in the bath by chemical or electro-chemical action.

The fused salt baths which may be used in the practice of my invention may vary considerably in com-

position. For example, the fused salt bath may be composed, in addition to the titanium halide, of one or a mixture of the chlorides, bromides, iodides and fluorides of alkali metals such as sodium and potassium. The titanium halide may be a chloride, bromide, iodide or fluoride and may be a simple halide or a complex halide such as a double fluoride of titanium and an alkali metal (also known as an alkali metal fluotitanate). The titanium halide should be present in the bath in the amount of at least about 5% by weight and generally up to about 25% by weight. The presence of fluorine in the bath in the form of such an alkali metal-titanium double fluoride, or of a simple alkali metal fluoride, promotes the formation of larger particles of cathodically deposited titanium than that which is obtained by any one or a mixture of the other halides. Except for this special effect of an added fluoride, the specific composition of the bath appears to have no effect upon the quality of the titanium metal deposited. Illustrative bath compositions which are useful in the practice of the invention are set forth in the following table, the numerical values under each salt heading representing the parts by weight or percentage of each component in the bath:

K <sub>2</sub> TiF <sub>6</sub>	NaCl	KCl
5	95	—
10	90	—
15	84	—
10	45	45
5	30	20
10	20	—

The most important characteristic of fused salt baths used in the practice of the invention, other than that of their titanium halide content, is that they be anhydrous and therefore oxygen-free. The alkali metal chlorides may be readily dehydrated by vacuum drying at a temperature of at least 120°C. or by heating the chlorides in a current of warm air at temperatures of about 300°-350°C. The alkali metal-titanium double fluorides may be dried by heating them at a temperature within the range of about 80° to 350°C., and preferably at a temperature within the lower portion of this range, under active vacuum pumping conditions. Whenever the salt components of the bath are dehydrated by vacuum drying, it is advantageous to start the drying operation at room temperature and gradually raise the temperature to the aforementioned values while maintaining active vacuum pumping. Once the salts have been rendered anhydrous, they may be kept in closed containers until ready for use without intervening adsorption or absorption of any significant amount of moisture.

The purity of the fused salt baths is also of importance inasmuch as any impurity introduced into the bath is a potential contaminant of the deposited titanium metal. The alkali metal halides are readily available in commercial quantities in a state of purity wholly adequate for use in the practice of the invention, but the alkali metal-titanium double fluoride, if of commercial grade, should be further purified by a single recrystallization operation. Such recrystallization may be effected by dissolving the double fluoride in hot water and by subsequently cooling the resulting solution to effect recrystallization of the double fluoride. The double fluoride crystals are advantageously washed with water containing a few per cent of potassium chloride, the latter tending to minimize loss of the double

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16	84	-
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containing a few per cent of potassium chloride, the latter  
tending to minify loss of the double fluoride by resolu-  
tion in the wash water. With the anhydrous nature and  
high degree of purity of the bath components thus assured,  
5 no further precautions need be taken in preparing the  
fused salt bath other than to maintain these conditions  
by the provision of a suitable inert atmosphere, such as  
argon or helium, during the melting down of these compon-  
ents.

10 The bath temperatures required for effective  
deposition of titanium from such a titanium halide  
containing bath are those which are at least  $50^{\circ}\text{C}.$  and  
preferably  $100^{\circ}\text{C}.$ , above the melting point of the bath.  
I have found that operating bath temperatures between  
15  $800^{\circ}$  and  $1000^{\circ}\text{C}.$  can be used with particularly satis-  
factory results.

The titanium nitride required for the practice  
of the invention is readily obtainable in sufficiently  
pure form, as a golden brown or tan lustrous powder.

20 The titanium nitride may be added to the bath  
directly, in finely divided form, or, if desired it may  
be converted into a more massive form such as a pellet,  
or even an anode. To accomplish this, the powder is  
transformed into a plastic, moldable material by admixing  
25 it with a small amount of water and a plasticizer such  
as, for example, methyl cellulose. I have found that a  
mixture of between 1 to 2 parts of methyl cellulose and  
100 parts by weight of titanium nitride may be converted  
into the desired extrudable mixture by the addition of a  
30 sufficient amount of water to form a plastic mixture

which, when extruded through a die, will retain its extruded shape during subsequent firing. After being shaped to a form suitable for use as an anode in an electrolytic cell, the titanium nitride mixture is fired to a temperature at which active sintering and possibly recrystallization takes place. This firing may be either in an inert atmosphere or under a vacuum. In the latter, care must be taken not to reach temperatures of 2000°C. or above, since the nitride tends to decompose in a vacuum at these temperatures.

The titanium nitride may be brought into contact with the fused salt bath in a variety of cell arrangements. If the titanium nitride is provided in the form of a finely divided powder, or in the form of lumps or pellets, the nitride may rest on the bottom of a graphite crucible holding the fused salt bath with the anode connection being made to the graphite crucible. A solid cathode suspended in the bath and a source of potential impressed across the electrodes completes the circuit. In another arrangement, the nitride is shaped into the form of a rod or plate or other preformed shape, and is supported in contact with the fused bath. The graphite crucible containing the bath is electrically neutral in this arrangement. Alternately the shaped anode may be fitted into slots or grooves in the crucible, and the crucible made anodic. Still another arrangement may be to charge lumps or pellets into a confined region adjacent the anode, and electrically connected thereto, as in a basket which functions as the anode. The electrodeposited titanium metal is advantageously deposited on a cathode

of titanium, molybdenum, nickel, iron or stainless steel. Other cathode materials may be employed provided they do not undesirably contaminate the titanium deposit under prevailing operating conditions.

5                   Decomposition of the titanium nitride during electrolysis proceeds with the deposition of metallic titanium on the cathode and the evolution of nitrogen at the anode. To prevent the nitrogen from recombining with the freshly deposited titanium, a shield or hood  
10                   may be suspended above the anode for withdrawal of the evolved nitrogen. Preferably the lower end of the hood is immersed in the fused bath, whereby the anode and cathode are effectively separated. It is usually desirable to operate the hood under a slight vacuum so as to with-  
15                   draw nitrogen from the atmosphere above the bath as rapidly as it forms.

                  The electrolysis is carried out under a purified noble gas, from which all oxygen hydrogen, water vapor, nitrogen and the like have been eliminated by conventional  
20                   techniques well known in the art. The voltage and current density are established and maintained below those at which any significant decomposition of the fused bath occurs, and more particularly, below those at which free  
25                   alkali metal is evolved and/or deposited and should be maintained at least as great as that required for the decomposition of the nitride and the deposition of  
titanium on the cathode. Cathode current densities of between about 25 and 500 amperes per square decimeter have been found suitable at voltages of 0.8 - 3.5 volts.

30                   The cathodically deposited titanium metal is



formed as a tightly adhering mixture of a densely deposited and well-crystallized metal and adhering salt. The cathode is periodically drawn into a separate cell chamber so that it may be cooled out of contact with air, whereupon a fresh cathode is immediately inserted in its place. After cooling of the withdrawn cathode is completed, the cathode deposit is knocked off and is disintegrated by treatment with hot water. The disintegrated cathode deposit is washed several times until substantially all of the salt has been removed, and the final washings are completed by treatment of the resulting powdered metal with dilute acid such as hydrochloric acid, followed by further washings with water and a final treatment with acetone, after which the powdered metal is dried under vacuum. It may then be compressed and fused either under a vacuum or under a controlled atmosphere of argon or helium to form a massive ingot.

The recovery of titanium from the nitride is quite high. In a typical run over 60% of the titanium contained in the nitride was deposited on the cathode in a single campaign. The remainder of the titanium remains as a bath constituent which ultimately becomes a fixed quantity under uniform cell conditions, with the result that the efficiency of the metal yield increases substantially after the first campaign. The titanium appears to deposit at the cathode by a direct electrochemical reaction in a manner characteristic of conventional electroplating and in actual operation no halogen is given off from the cell under normal operating conditions. The evolution of free halogen is, indeed, a warning that

existing cell conditions are improper.

In view of the fact that a titanium nitride anode is consumed during electrolysis pursuant to the practice of this invention, anode effects are not encountered. Thus, cathode current densities ranging from 25 to 500 amperes per square decimeter can be used without untoward results, the upper limit being determined by the fact that at significantly higher current densities undue overheating of the cell and the formation of free alkali metal occur. Within the aforementioned range of current densities, I presently prefer to control the cell voltage and operating temperature within the aforementioned ranges so as to establish a current density of about 50 to 150 amperes per square decimeter.

The following specific examples are illustrative of the practice of my invention.

EXAMPLE I

A fused salt bath was prepared by melting a mixture composed of 84% by weight of anhydrous NaCl and 16% by weight of recrystallized, vacuum dried  $K_2TiF_6$  in a graphite crucible. The crucible was connected to a source of potential, so as to serve as the anode. After the melt was held at  $850^{\circ}C$ . for about three hours, 30 grams of titanium nitride in the form of a powder was added to the melt. A steel cone-shaped cathode was inserted in the melt and an electrolysis was conducted under a current of purified argon which flowed continuously through the cell and which carried off the nitrogen evolved as a result of the electrolysis. The electrolysis was run for a total of 124 ampere hours at 3.0 volts and 60-70

amperes (DC), which was equivalent to a cathode current density of 133-145 amperes/square decimeter. The bath was maintained at temperature by means of an external heating element. When a rise in voltage occurred, the electrolysis was terminated.

The resultant deposit had a smooth outer surface and was shiny black in color. The inner portion of the deposit was dark gray in color. The deposit was chipped from the steel cathode and washed in an acidified wash water to remove entrained bath material. The nitrogen content of the unconsolidated metal was 0.046% N. The salt cake resulting from allowing the bath to freeze was shattered with a hammer. A characteristic dark lavender color was noted, evidence of the presence of titanium in the form of di- or trivalent material, in contrast with the original bath which when cold, solidifies as a milky white solid.

When freed of extraneous material, the metal was dried and was then vacuum melted to produce a button. Twenty grams of metal having a Brinell Hardness of 155 was obtained. The metal recovered represented a yield of 86% based on the original titanium present in the nitride. The resulting powder was melted into an ingot under an argon atmosphere and the ingot, which contained less than 0.1% oxygen, had a Rockwell A Hardness of 53.

#### EXAMPLE II

The operation described in Example I was repeated with the exception that the titanium nitride was formed into a rod shaped anode and the crucible was made neutral instead of anodic. The electrolysis was carried

out for a total of 150 ampere hours, after which the cathode was removed and the metal recovered therefrom.

EXAMPLE III

5 The operation described in Example II was repeated, employing a bath consisting of about 15 parts by weight of potassium titanium fluoride and 100 parts by weight of a eutectic composition of sodium chloride and potassium chloride. The bath was electrolyzed at a temperature of about 850°C. The results obtained were not  
10 materially different from those of Example II.

The method of producing titanium metal by electrolysis of titanium nitride pursuant to my invention is characterized by a high degree of purity in the electro-  
15 deposited titanium. The complete absence of oxygen and carbon and other potential contaminants in the nitride anode and the anhydrous character of a fused salt bath preclude the presence of excessive amounts of oxygen in the cathode deposit. Massive titanium metal obtained  
20 by melting down the aforementioned cathode deposits under noncontaminating conditions, is sufficiently ductile to permit cold rolling to sheet form.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal chloride, maintaining the fused electrolyte bath under an inert atmosphere, providing solid titanium nitride as the source of titanium in said bath, providing a solid deposition cathode, providing an electrical circuit whereby said nitride is electrically connected to the anode in said cell and is thereby made anodic in the electrolysis which follows, passing an electrolyzing current through the fused bath and thereby electrolytically decomposing the titanium nitride and recovering the resultant cathodically deposited titanium metal.

2. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal chloride and up to 25% by weight of a halide of titanium, maintaining the fused electrolyte bath under an inert atmosphere, providing solid titanium nitride as the source of titanium in said bath, providing a solid deposition cathode, providing an electrical circuit whereby said nitride is electrically connected to the anode in said cell and is thereby made anodic in the electrolysis which follows, passing an electrolyzing current through the fused bath and thereby electrolytically decomposing the titanium nitride and recovering the resultant cathodically deposited titanium metal.

3. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal chloride, maintaining the fused electrolyte bath under an inert atmosphere, providing a titanium nitride anode in contact with the bath as the source of titanium in said bath, providing a solid deposition cathode, passing an electrolyzing current through the fused bath and thereby electrolytically decomposing the titanium nitride and recovering the resultant cathodically deposited titanium metal.

4. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal chloride, maintaining the fused electrolyte bath under an inert atmosphere, providing solid titanium nitride as the source of titanium in said bath, providing a solid deposition cathode, providing an electrical circuit whereby said nitride is electrically connected to the anode in said cell and is thereby made anodic in the electrolysis which follows, passing an electrolyzing current through the fused bath to maintain a cathode current density between about 25 and 500 amperes per square decimeter and thereby electrolytically decomposing the titanium nitride and recovering the resultant cathodically deposited titanium metal.

5. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting essentially of at least one alkali metal chloride, providing solid titanium nitride as the source of titanium in said bath, providing an electrical circuit wherein said nitride is made anodic in the electrolysis which follows, providing a solid deposition cathode, passing an electrolyzing current through the bath to maintain a cathode current density of between about 25 and 500 amperes per square decimeter and thereby decomposing the titanium nitride, to form nitrogen at the anodic electrode and titanium as a cathode deposit, while maintaining an inert atmosphere above the fused salt cell bath, and providing a means to confine the nitrogen evolved to a region immediately adjacent the anode and a means to effect withdrawal of the nitrogen from the inert atmosphere maintained above the salt bath.

(31)

6. The method of producing metallic titanium in an electrolytic cell which comprises: preparing a fused electrolyte consisting of at least one salt from the group of alkali metal halides and alkali metal fluotitanates, maintaining the fused electrolyte bath under an inert atmosphere, providing as the source of titanium in said bath solid titanium nitride connected as an anode, providing a solid deposition cathode, passing an electrolysing current through the fused bath and thereby electrolytically decomposing the titanium nitride and recovering the resultant cathodically deposited titanium metal.

(C3)

7. A process according to Claim 6 in which the electrolyte contains a fluoride.

(C4)

8. A process according to Claim 6 in which there is included in the electrolyte at the commencement of electrolysis a quantity of at least one member of the group consisting of titanium dichloride and titanium trichloride.

(C5)

9. A process according to Claim 8 in which the quantity of titanium chloride included in the electrolyte is such that the titanium content of the electrolyte in the form of subchlorides is between 3% and 5% by weight.



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